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DESCRIPTION

POLYBENZAZOLE FIBERS AND ARTICLES MADE THEREOF

FIELD OF THE INVENTION

The present application has been filed claiming the priority based on the Japanese patent application Nos. 2003-412681, 2003-424648, 2003-424649, 2003-424650, 2003-424651, 2003-424652, 2003-424653, 2003-424654 and 2003-424655, and a whole of the descriptions of these applications are herein fully incorporated in the description of the present specification by reference.

The present invention relates to polybenzazole fibers which can still have high durability against atmospheres of high temperatures and high humidity even after yarns made thereof have had kink bands therein due to the damages in the course of post-processing for making woven fabrics, knitted fabrics, braids, ropes and cords. The invention also relates to articles comprising the polybenzazole fibers, particularly spun yarns, rubber-reinforcing materials, fiber-reinforced composite materials, woven or knitted fabrics, knife-proof materials or bullet-proof vests, ropes and sail cloths.

BACKGROUND OF THE INVENTION

As high strength and high heat resistant fibers, there are known polybenzazole fibers comprising a polybenzoxazole or a polybenzothiazole, or a copolymer thereof.

In general, the filaments of polybenzazole are obtained by extruding a dope containing the above polymer or copolymer and an acid solvent through a spinneret, dipping the resulting semi-solid filaments in a fluid for

solidifying them (water, or a mixture of water and an inorganic acid) to solidify them, thoroughly washing the solid filaments in a water bath to remove most of the solvent therefrom, allowing the filaments to pass through a bath holding an aqueous solution of an inorganic base to thereby neutralize the acid which has not been extracted and still remained in the filaments, and drying the same.

Polybenzazole fibers have been variously applied, because they are excellent in mechanical properties such as strength and also have high heat resistance. Lately, the polybenzazole fibers are expected to have further improved performance. Particularly desired are such polybenzazole fibers that can still have high durability against atmospheres of high temperatures and high humidity even after yarns made thereof have had kink bands therein due to the damages in the course of post-processing for making articles comprising the same, such as woven fabrics, knitted fabrics, braids, ropes and cords. In other words, such polybenzazole fibers are earnestly desired that can sufficiently maintain the strength thereof even after exposed to atmospheres of high temperatures and high humidity over long periods of time.

For example, spun yarns made of the polybenzazole fibers are known. However, such spun yarns are demanded to have further improved performance. Particularly desired are such polybenzazole fibers that can still have durability against atmospheres of high temperatures and high humidity even after yarns made of the same have had kink bands therein due to damages which occur in the course of post-processing for making woven or knitted fabrics, braids, ropes, cords, etc. of such yarns. In other words, such polybenzazole fibers are strongly demanded that can

sufficiently maintain the strength thereof even after exposed to atmospheres of high temperatures and high humidity over long periods of time.

Conventionally, nylon fibers, polyester fibers, glass fibers and steel fibers have been mainly used as rubber-reinforcing materials for tires, hoses, belts and the like. Recently, aromatic polyamide fibers having high strength and high elastic modulus, such as KEVLAR, have been used as reinforcing materials for a variety of rubbers. Under these circumstances, the use of the polybenzazole fibers as rubber-reinforcing materials have attracted keen public attentions, because the polybenzazole fibers have far higher strength and elastic modulus and higher heat resistance and dimensional stability than the aromatic polyamide fibers. Under such a situation, investigations have been made on the use of the polybenzazole fibers as rubber-reinforcing fibers which are required to have still higher strength and heat resistance that the organic fibers conventionally used in the field of rubber materials can not possess.

Under such circumstances, particularly desired are such polybenzazole fibers for reinforcing rubber, that can sufficiently maintain the strength thereof, when the internal solid of rubber has high temperature and high humidity because of the dynamic fatigue applied to the rubber-reinforcing material.

Glass fibers have hitherto been used in fiber-reinforced composite materials. Recently, composite materials comprising carbon fibers or aramid fibers have been developed in order to improve the strength of the composite materials and reduce the weight thereof, and such composite materials have been practically used. Carbon

fibers, however, have a problem in their poor impact resistance and fragility, although having very excellent dynamical performance. Aramid fibers have relatively high impact resistance, but have a lower elastic modulus than the carbon fibers and thus are poor in reinforcing effect. Under these circumstance, fiber-reinforced composite materials comprising the polybenzazole fibers are expected as the products of the next generation, since they are excellent in both of impact resistance and elastic modulus, exhibiting a superior reinforcing effect over the carbon fibers.

However, the fiber-reinforced composite materials comprising the polybenzazole fibers are demanded to have further improved performance. Particularly desired is a fiber-reinforced composite material which comprises such polybenzazole fibers that can sufficiently maintain the strength thereof when exposed to an atmosphere of high temperature and high humidity over a long period of time.

As mentioned above, the polybenzazole fibers have high mechanical properties such as strength and elastic modulus, and therefore are used as fibrous materials for protective materials, protective clothes and industrial materials. However, woven or knitted fabrics comprising the polybenzazole fibers are demanded to have further improved performance. Particularly desired is a woven or knitted fabric comprising such polybenzazole fibers that can sufficiently maintain the strength thereof when exposed to an atmosphere of high temperature and high humidity over a long period of time.

Conventionally, aramid fibers have been used to make knife-proof materials or bullet-proof vests, and recently, knife-proof materials or bullet-proof vests made of high

strength polyethylene fibers have been developed and put into practical use. The knife-proof materials or bullet-proof vests made of the aramid fibers require lots of the fibers to exhibit the desired protective performance, and thus are thick and heavy in weight and are uncomfortable to wear. Therefore, ones can not always wear them. On the other hand, knife-proof materials or bullet-proof vests made of high strength polyethylene fibers are reduced in weight but not in thickness because of the small specific gravity of the fibers. Under these circumstances, knife-proof materials or bullet-proof vests made of the polybenzazole fibers can exhibit superior protective performance over the knife-proof materials or bullet-proof vests made of the aramid fibers and the high strength polyethylene fibers, and are expected as thin and light weight knife-proof materials or bullet-proof vests of the next generation.

However, the knife-proof materials or bullet-proof vests made of the polybenzazole fibers are demanded to have further improved performance. Particularly desired is a knife-proof materials or bullet-proof vest made of such polybenzazole fibers that can sufficiently maintain the strength thereof when exposed to an atmosphere of high temperature and high humidity over a long period of time.

Since the polybenzazole fibers have high mechanical properties such as strength and also have high heat resistance as mentioned above, they have been widely used in ropes, including yacht ropes, which are required to have strength and abrasion resistance. However, the polybenzazole fibers are susceptible to mechanical damages in the course of manufacturing of ropes, since they have very highly oriented molecular chain structures. To

overcome this problem, there is a demand for such polybenzazole fibers that can still have high durability against atmospheres of high temperatures and high humidity even after yarns made thereof have had kink bands therein due to the damages in the course of post-processing for making ropes and cords, in other words, such polybenzazole fibers that can sufficiently maintain the strength thereof even when exposed to atmospheres of high temperatures and high humidity over long periods of time.

Sail cloths comprising the polybenzazole fibers also have been widely used. Particularly, yacht sails for use in yacht races are demanded to have high tensile resistance and high tensile strength so as not to permit their designed shapes to deform due to winds. To solve this problem, such a sail cloth is dominantly used that is made by sandwiching a woven fabric or a scrim which comprises fibers having high strength and a high elastic modulus, between two films of polyester or the like to form their lamination, and molding the lamination into the sail cloth. Further, a method of making a yacht sail as an integral three-dimensional molded article has been developed. Such an integral three-dimensional molded article is also included in the scope of the sail cloth referred to in the description of the present invention. Conventionally, para-aramid fibers or carbon fibers have been used to make these products by employing the above technique. Carbon fibers have a higher tensile elastic modulus than para-aramid fibers, and thus are expected to improve the performance of a yacht sail made thereof, but are easily bent and thus are inferior in fatigue resistance. To overcome these problems, yacht sails comprising the polybenzazole fibers have been developed, and such yacht

sails have proved their excellent performance in the world-wide yacht races.

However, the yacht sails comprising the polybenzazole fibers are demanded to have further improved performance. Especially desired is a yacht sail made of such polybenzazole fibers that can sufficiently maintain the strength thereof when exposed to an atmosphere of high temperature and high humidity over a long period of time.

DISCLOSURE OF THE INVENTION

Subject Matter to be Achieved by the Invention

The present invention has been developed under the foregoing circumstances, and an object of the invention is to provide polybenzazole fibers which show less decrease in strength, even after yarns made thereof have had kink bands therein due to damages thereof, and even after the fibers have been exposed to atmospheres of high temperatures and high humidity over long periods of time.

Another object of the present invention is to provide articles comprising the polybenzazole fibers, such as spun yarns, woven or knitted fabrics, rubber-reinforcing materials, fiber-reinforced composite materials, ropes, sail cloths, and knife-proof materials or bullet-proof vests.

Means for Achieving the Subject Matter

The present invention provides the followings.

1. A polybenzazole fiber having a strength retention (%) of 80% or more, which is determined by the equation: (**a**/**b**) X 100, provided that the notations **a** and **b** are defined as follows:

the notation **a** indicates the strength of a yarn [cN/dtex] measured as follows: polybenzazole filaments are S-wise

twisted so that the twist coefficient can be 30, to thereby make a yarn, which is then left to stand alone for 30 seconds, and the yarn is S-wise untwisted until the twist coefficient is decreased to 6, and the untwisted yarn is exposed to an atmosphere of 80°C and 80 RH% for 240 hours and taken out at room temperature to measure the strength of the yarn; and

the notation **b** indicates the strength of a yarn [cN/dtex] measured as follows: polybenzazole filaments are S-wise twisted so that the twist coefficient can be 30, to thereby make a yarn, which is then left to stand alone for 30 seconds, and the yarn is S-wise untwisted until the twist coefficient is decreased to 6, and the strength of the untwisted yarn is measured.

2. A polybenzazole fiber according to the above paragraph 1, wherein the average strength of a single polybenzazole fiber with an average diameter D of 5 to 22 μm and a length of 100 mm is 4.5 GPa or more.

3. A polybenzazole fiber according to the above paragraph 1, wherein the coefficient of variation CV (a standard deviation/an average value) of the diameters of a single filament, measured at 10 mm intervals over 500 mm length of the filament is 0.08 or less.

4. A polybenzazole fiber according to the above paragraph 1, wherein the stoichiometric ratio of an inorganic base to a mineral acid remaining in the fiber is 0.8 to 1.4 : 1.

5. A polybenzazole fiber according to the above paragraph 1, which contain an organic pigment having a thermal

decomposition temperature of 200°C or higher and soluble in a mineral acid.

6. A polybenzazole fiber according to the above paragraph 5, wherein the content of the organic pigment is 2 to 8 mass %.

7. A spun yarn comprising a polybenzazole fiber according to any of the above paragraphs 1 to 6, as at least one component.

8. A cord for reinforcing rubber, comprising a polybenzazole fiber according to any of the above paragraphs 1 to 6, as at least one component.

9. A composite material comprising a polybenzazole fiber according to any of the above paragraphs 1 to 6, as at least one component.

10. A woven or knitted fabric comprising a polybenzazole fiber according to any of the above paragraphs 1 to 6, as at least one component.

11. A knife-proof material comprising a polybenzazole fiber according to any of the above paragraphs 1 to 6, as at least one component.

12. A bullet-proof vest comprising a polybenzazole fiber according to any of the above paragraphs 1 to 6, as at least one component.

13. A high strength fiber rope comprising a polybenzazole

fiber according to any of the above paragraphs 1 to 6, as at least one component.

14. A sail cloth comprising a polybenzazole fiber according to any of the above paragraphs 1 to 6, as at least one component.

The present inventors have discovered the following facts and accomplished the present invention.

(1) The durability of a yarn made of fibers containing a specified amount of an organic pigment which has heat resistance as high as a thermal decomposition temperature of 200°C or higher and is soluble in a mineral acid, and which preferably has group(s) of -N= and/or NH- in the molecule and which is selected from perinones and/or perylenes, phthalocyanines and quinacridones, under an atmosphere of high temperature and high humidity, is improved, and the strength of such a yarn very hardly decreases even after the yarn has had kink bands therein due to the damages thereof, more specifically, even after the yarn has been exposed to an atmosphere of high temperature and high humidity over a long period of time, as compared with a yarn made of fibers not containing such an organic pigment.

(2) The durability of a yarn made of polybenzazole fibers, under an atmosphere of high temperature and high humidity is improved, even after the yarn has had a kink band therein due to damages, by maintaining the pH of the internal of the yarn at and around 7, which is a very important factor. Specifically, the strength of such a yarn very hardly decreases even after the exposure to an atmosphere of high temperature and high humidity over a

long period of time.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 shows an example of a resin-impregnating apparatus with a die for making a composite material comprising the polybenzazole fibers of the present invention. In the drawing, A refers to a filament; B, to an introduction angle; C, to the diameter of a nozzle; D, to the length of the parallel portion; and E, to a die.

BEST MODES FOR CARRYING OUT THE INVENTION

Hereinafter, the present invention will be described in more detail.

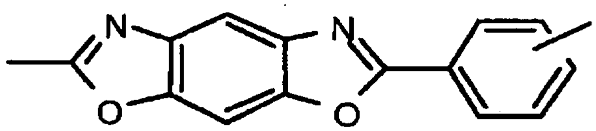
The polybenzazole fibers according to the present invention means fibers which comprise a polybenzazole polymer. The polybenzazole polymer (hereinafter referred to as PBZ) is at least one polymer selected from the group consisting of polybenzoxazole (hereinafter referred to as PBO), polybenzothiazole (hereinafter referred to as PBT) and polybenzimidazole (hereinafter referred to as PBI).

In the present invention, PBO means a polymer which contains an oxazole ring bonded to an aromatic group which is not necessarily a benzene ring. Examples of PBO include lots of polymers each of which comprises a unit of a plurality of oxazole rings bonded to poly(p-phenylenebenzbisoxazole) or an aromatic group. Analogous structures are also applied to PBT and PBI.

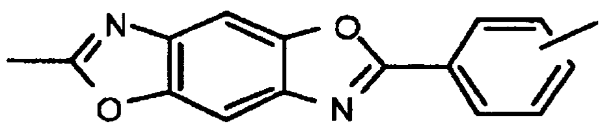
Examples of the polybenzazole polymer of the present invention also include optional mixtures of PBO, PBT and PBI, and block or random copolymers each of which comprises at least two of PBO, PBT and PBI.

The structural unit in the PBZ polymer is preferably

selected from lyotropic liquid crystalline polymers which form liquid crystals in mineral acids at specified concentrations. Such a polymer comprises a monomer unit of any of the following structural formulas (a) to (f):



(a)



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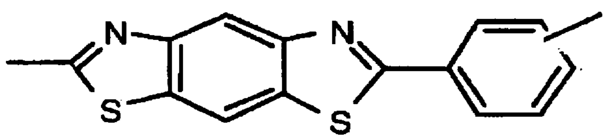

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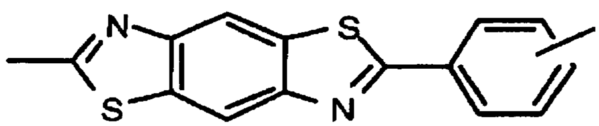

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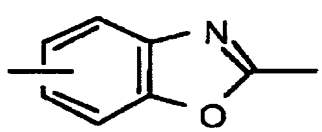
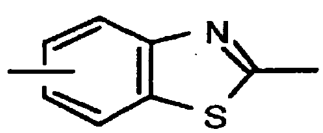


(e)



(f)

The polybenzazole fibers can be manufactured from a dope containing a PBZ polymer. As a suitable solvent for preparing this dope, cresol or a non-oxidizing acid capable of dissolving the polymer is used. Preferred examples of the non-oxidizing acid include polyphosphoric acid,

methanesulfonic acid, highly concentrated sulfuric acid, and mixtures thereof. Above all, polyphosphoric acid and methanesulfonic acid are preferred, and polyphosphoric acid is especially preferred.

The concentration of the polymer in the dope is preferably at least about 7 mass %, more preferably at least 10 mass %, particularly at least 14 mass %. The maximum concentration of the polymer is limited depending on the practical handling ease of the dope, for example, the solubility of the polymer or the viscosity of the dope. Because of such restrictive factors, the concentration of the polymer is generally not higher than 20 mass %.

In the present invention, a suitable polymer or copolymer and a suitable dope can be prepared by any of known methods, for example, described in the publications of U.S. Patent No. 4,533,693 by Wolfe et al. (August 6, 1985), U.S. Patent No. 4,772,678 by Sybert et al. (September 22, 1988), U.S. Patent No. 4,847,350 by Harris (July 11, 1989) and U.S. Patent No. 5,089,591 by Gregory et al. (February 18, 1992).

According to the above patent literature, a suitable monomer is reacted in a non-oxidizing and dehydrating acid solution under a non-oxidizing atmosphere, while being stirred at high speed under a high shearing condition, at a temperature which is increased stepwise or at a constant rate from about 60°C to about 230°C, to thereby form a dope.

The dope thus obtained is extruded through a spinneret, and the resulting semi-solid filaments are drawn long in an air to thereby form solid filaments. The preferred methods therefor are described in the above literature and the publication of U.S. Patent No. 5,034,250. In particular, the dope extruded through the spinneret is allowed to pass

through a space between the spinneret and the washing bath. This space is called an air gap, and is generally charged with a gas such as an air, nitrogen, argon, helium, carbon dioxide or the like, or may be charged with a liquid which does not dissolve the solvent or react with the dope.

The filaments resulting from the spinning are washed so as not to be excessively drawn, and a part of the solvent is removed. The filaments are further washed and neutralized with a suitable inorganic base such as sodium hydroxide, calcium hydroxide, potassium hydroxide or the like to thereby remove most of the solvent. The washing herein referred to means that the fibers or the filaments are allowed to contact a liquid which is compatible with a mineral acid dissolving the polybenzazole polymer and which does not serve as a solvent for the polybenzazole polymer, to thereby remove the acid solvent from the dope. As a preferable washing liquid, water or a mixture of water with an acid solvent is used. Preferably, the filaments are washed until the concentration of the residual mineral acid reached 8,000 ppm or less, preferably 5,000 ppm or less. After that, the filaments are dried and heat-treated, and if needed, are wound up.

As the organic pigment which has heat resistance as high as a thermal decomposition temperature of 200°C or higher and which is dissolved in a mineral acid, there can be used any of organic pigments that can be left to remain in the fibers or filaments when added in the course of the polymerization or added to a polymer dope and involved in the spinning from the such a dope. Specific examples of such an organic pigment include insoluble azo pigments, condensed azo pigments, color lakes, isoindolinones, isoindolines, dioxazines, perinones and/or perylenes,

phthalocyanines, quinacridones and the like. Among those, preferred are the organic pigments each having group(s) of -N= and/or NH- in the molecule, and more preferred are perinones and/or perylenes, phthalocyanines and quinacridones.

Examples of perinones and/or perylenes include bisbenzimidazo[2,1-b:2',1',i]benzo[lmn][3,8]phenanthroline-8,17-dione, bisbenzimidazo[2,1-b:1',2'-j]benzo[lmn][3,8]phenanthroline-6,9-dione, 2,9-bis(p-methoxybenzyl)anthora[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron, 2,9-bis(p-ethoxybenzyl)anthora[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron, 2,9-bis(3,5-dimethoxybenzyl)anthora[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron, 2,9-bis(p-methoxyphenyl)anthora[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron, 2,9-bis(p-ethoxyphenyl)anthora[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron, 2,9-bis(3,5-dimethylphenyl)anthora[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron, 2,9-dimethylanthora[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron, 2,9-bis(4-phenylazophenyl)anthora[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10(2H,9H)-tetron, 8,16-pyranthrenedione, etc. Each of these perinones may be used alone or in combination.

As the phthalocyanines, any of phthalocyanines that have phthalocyanine backbones may be used, independently of the presence or absence of a metal at the center of the ligand and the kind of an atom. Specific examples of these compounds are 29H,31H-phthalocyanate(2-)-N29,N30,N31,N32

copper, 29H,31H-phthalocyanate(2-)-N29,N30,N31,N32 iron, 29H,31H-phthalocyanate-N29,N30,N31,N32 cobalt, 29H,31H-phthalocyanate(2-)-N29,N30,N31,N32 copper, oxo(29H,31H-phthalocyanate(2-)-N29,N30,N31,N32),(SP-5-12) titanium, etc. The backbone of each of these phtalocyanines may have at least one substituent such as a halogen atom, methyl group, methoxy group or the like. Each of these phthalocyanines may be used alone or in combination.

Examples of the quinacridones include 5,12-dihydro-2,9-dimethylquino[2,3-b]acridine-7,14-dione, 5,12-dihydroquino[2,3-b]acridine-7,14-dione, 5,12-dihydro-2,9-dichloroquino[2,3-b]acridine-7,14-dione, 5,12-dihydro-2,9-dibromoquino[2,3-b]acridine-7,14-dione, etc. Each of these quinacridones may be used alone or in combination.

Further, each of the above perylenes, perinones, phthalocyanines and quinacridones may be used in combination with at least another one or more selected therefrom.

There is no particular limit in selection of the method for containing the above organic compound in the filaments. The organic compound may be added in any of the steps for the polymerization of polybenzazole, or may be added to a polymer dope obtained after completion of the polymerization. For example, the organic pigment may be added together with the starting materials for polybenzazole, or may be added in some stages or at an optional point of time during the reaction which proceeds while the reaction temperature is being raised at an optional rate. Otherwise, the organic pigment may be added to the reaction system after completion of the polymerization, and stirred and mixed into the reaction system.

The most distinguishing feature of the polybenzazole fibers of the present invention is that a yarn made of the polybenzazole fibers by twisting at a twist coefficient of 30 can have a strength retention of 80% or more after exposed to an atmosphere of 80°C and 80RH% for 240 hours. The polybenzazole fibers of the present invention shows a strength retention of 80% or more, defined by the equation of (**a**/**b**) X 100.

In the above equation, the notation **a** means strength [cN/dtex] measured as follows. The filaments are S-wise twisted until the twist coefficient can be 30, to thereby make a S-twisted yarn, which is then left to stand alone for 30 seconds. The yarn is then S-wise untwisted until the twist coefficient is decreased to 6. The untwisted yarn is exposed to an atmosphere of 80°C and 80 RH% for 240 hours, and is taken out to an atmosphere of a room temperature to measure the strength thereof.

The notation **b** means strength [cN/dex] measured as follows. The filaments are S-wise twisted until the twist coefficient can be 30, to thereby make a S-twisted yarn, which is then left to stand alone for 30 seconds. The yarn is then S-wise untwisted until the twist coefficient is decreased to 6. Then, the strength of the untwisted yarn is measured.

The strength retention (%) of the polybenzazole fibers of the present invention is preferably 80 to 100%, more preferably 82 to 100%, still more preferably 84 to 100%, far more preferably 85 to 100%, specifically 80 to 99%, and more specifically 80 to 98%, still more specifically 84 to 98%.

Since the molecules of the polybenzazole fibers have high rigidity and the interaction between each of the

molecular chains is low, kink bands occur in directions vertically to the axial directions of the polybenzazole fibers when a bending stress is applied to the polybenzazole fibers. While the degrees of the kink bands differ depending on the kinds of post processing, kink bands usually occur in fibers which have undergone post processing. Kink bands also occur in fibers which are simply twisted, if the number of twists is increased. The polybenzazole fibers having had kink bands therein show larger decrease in the strength thereof when exposed to an atmosphere of high temperature and high humidity over a long period of time, as compared with polybenzazole fibers having no kink band therein. However, this disadvantage can be solved by containing any of the above organic pigments in the filaments after spinning. That is, the polybenzazole filaments containing the organic pigment, even though having kink bands therein, show higher durability against an atmosphere of high temperature and high humidity, namely, shows a less decrease in the strength thereof when exposed to such an atmosphere over a long period of time. Thus, the yarns of the polybenzazole fibers which are damaged to have kink bands therein in the course of the post processing for making woven fabrics, knitted fabrics, brads, ropes, cords or the like, show high durability against atmospheres of high temperatures and high humidity. The organic pigment herein referred to means such an organic pigment that has heat resistance as high as a thermal decomposition temperature of 200°C or higher and is soluble in a mineral acid, and preferably has group(s) of -N= and/or NH- in the molecule. More preferably, such an organic pigment is selected from perinones and/or perylenes, phthalocyanines and

quinacridones.

Desirably, the polybenzazole fibers of the present invention have a stoichiometric ratio of an inorganic base to a mineral acid, remaining in the fibers, of 0.8 to 1.4 : 1. When the stoichiometic ratio of the inorganic base to the mineral acid in the fibers is too small, the pH inside of the fibers extremely inclines to the acidic side, which accelerates the hydrolysis of the PBZ molecules and lowers the strength of the fibers. This tendency becomes more remarkable in the polybenzazole fibers having kink bands therein, as compared with polybenzazole fibers having no kink band therein. Thus, the polybenzazole fibers having kink bands therein show larger decrease in strength when exposed to an atmosphere of high temperature and high humidity over a long period of time. On the other hand, when the stoichiometic ratio of the inorganic base to the mineral acid in the fibers is too large, the pH inside of the fibers extremely inclines to the basic side, which accelerates the hydrolysis of the PBZ molecules and lowers the strength of the fibers. This tendency becomes more remarkable in the polybenzazole fibers having kink bands therein, as compared with polybenzazole fibers having no kink band therein. Thus, the polybenzazole fibers having kink bands therein show larger decrease in strength when exposed to an atmosphere of high temperature and high humidity over a long period of time. For this reason, the stoichiometric ratio of the inorganic base to the mineral acid, remaining in the fibers, is preferably 0.8 to 1.4 : 1, more preferably 1.0 to 1.3 : 1. Desirably, this stoichiometic ratio can be found in any portions of the fibers. As the method of neutralizing the fibers with the inorganic base in the washing step, a guide oiling system,

showering system, dipping system or the like is employed. The method, however, is not limited to these.

The content of the above organic pigment in the polybenzazole fibers of the present invention is preferably 2 to 8 mass%, more preferably 3 to 6 mass%. When this content is too low, the effect of the organic pigment in the fibers becomes poor: namely, the effect of improving the durability of the fibers having had kink bands therein, specifically, the effect of suppressing the lowering of the strength of the fibers when such fibers have been exposed to an atmosphere of high temperature and high humidity over a long period of time, becomes poor. On the other hand, when this content is too large, the fineness of the polybenzazole filaments becomes larger, and such filaments have uneven thickness, which lowers the initial strength of the filaments. When this content is in the range of 2 to 8 mass%, the initial strength of the filaments does not decrease due to the presence of the organic pigment in the filaments, and the spinnable property of the dope is sufficient. Thus, smooth spinning can be maintained without any filament breakage. This may be because the pigment added is dissolved in the mineral acid and thus also still dissolved in the polymer dope. However, this speculation does not restrict the present invention in any way.

The polybenzazole fibers of the present invention has an average diameter D of 5 to 22 μm, more preferably 10 to 20 μm, as a single filament.

The average strength of the polybenzazole fibers is preferably 4.5 GPa or more, more preferably 5.0 to 8.0 GPa, provided that the length of the fiber is 100 mm.

The polybenzazole fibers of the present invention

preferably contain the organic pigment therein, as mentioned above. Therefore, sufficient control is needed to prevent the unevenness in the diameters of the fibers. The coefficient of variation CV (a standard deviation/an average value) of the diameters of a single polybenzazole filament of the present invention, measured at 10 mm intervals over a length of 500 mm, is preferably 0.08 or less, more preferably 0.06 or less. When the coefficient of variation CV is too large, a stress tends to concentrate on the thin portion of the fiber, so that the fiber is easily broken.

The polybenzazole fibers of the present invention show high durability against an atmosphere of high temperature and high humidity, and thus are variously and suitably used in the following articles. Particularly, the polybenzazole fibers of the present invention are suitably used in spun yarns, rubber-reinforcing materials, fiber-reinforced composite materials, woven or knitted fabrics, knife-proof materials or bullet-proof vests, ropes, sail cloths and the like.

The polybenzazole fibers of the present invention are suitably used in spun yarns, especially, spun yarns for use in fibrous structures of industrial materials for protective materials or protective clothing such as fireman uniforms, fire-resistant clothing and working wears, conveyer materials, cushion materials, coating protective materials, etc., which are all required to have high strength and high heat resistance.

The spun yarns of the present invention include composite spun yarns blended with other kinds of fibers. As other kinds of fibers, natural fibers, organic fibers, metal fibers, inorganic fibers, mineral fibers and the like

may be used. The method of blending fibers and the forms of yarns are not limited, and the generic method using opener and scutcher may be employed, or the composite yarn may be in the form of a yarn having a core-in-sheath structure.

The polybenzazole fibers of the present invention can be suitably used as rubber-reinforcing materials for tires, belts and hoses.

The polybenzazole fibers for use in rubber-reinforcing cords may be made into a single twist yarn or a two folded twist yarn with a ring twisting machine or the like, in order to improve the fatigue resistance. In this case, the twist coefficient (K) may be 10 to 100.

To improve the adhesivity of the polybenzazole fibers with rubber, the polybenzazole fibers may be surface-treated with corona or plasma. Further, a compound reactive with the surfaces of the polybenzazole fibers or the corona-treated surfaces of the polybenzazole fibers may be added to the polybenzazole fibers. To otherwise improve the adhesivity with rubber, the polybenzazole fibers may be subjected to a dipping treatment.

As the treating liquid, each of the following liquids may be generally used alone or in combination so as to treat the fibers in one stage or two or more stages, although any other method may be applicable: (A) an aqueous dispersion of an epoxy resin, (B) an aqueous dispersion of a blocked isocyanate, (C) an aqueous dispersion of a rubber latex, and (D) a liquid mixture of a resorcin/formaldehyde resin and a rubber latex (RFL).

The polybenzazole fibers of the present invention can be suitably used in composite material. The composite material comprising the polybenzazole fibers of the present

invention may be in any form of an unidirectionally reinforced material, a pseudoisotropic laminated layer and a fabric laminated layer. As a matrix resin, there may be used any of thermosetting resins such as an epoxy resin and a phenol resin, super engineering plastics such as PPS and PEEK, and general-purpose thermoplastic resins such as PE, PP and polyamide.

The polybenzazole fibers of the present invention can be suitably used in woven or knitted fabrics, particularly for protective materials for fireman uniforms, fire resistant clothing and working wears, and protective clothing which are required to have high strength and high heat resistance, and woven or knitted fabrics for industrial materials for use in conveyer materials, cushion materials and coating protective materials which are required to have high strength and high heat resistance.

The woven or knitted fabrics of the present invention include composite woven or knitted fabrics in combination with other kinds of fibers. As other kinds of fibers, natural fiber, organic fibers, metal fibers, inorganic fibers, mineral fibers and the like may be used. The combining method is not particularly limited. The kinds of the woven fabrics include union cloth, double woven cloth, lip stop, etc. The kinds of the knitted fabrics include union knitting, double knitting, tubular knitting, weft knitting, warp knitting, Raschel knitting, etc. The fiber bundles composing the woven or knitted fabric are not particularly limited, and examples thereof include monofilaments, multifilaments, twisted yarns, twisted union yarns, covering yarns, spun yarns, stretch broken yarns, yarns having a core-in-sheath structure, braids, etc.

The polybenzazole fibers of the present invention can

be suitably used in knife-proof materials for vests and gloves. The knife-proof material according to the present invention comprises a lamination of woven fabrics made of the polybenzazole fibers. As the texture of the woven fabric, any of a plain weave fabric, a twill fabric and other textures generally used in fabrics may be employed. Preferably, a plain weave fabric or a twill fabric in which yarns are hard to move is selected to attain higher knife-proof performance.

When the fineness of the polybenzazole fibers for use in the knife-proof material according to the present invention is as low as 600 dtex or less, preferably 300 dtex or less, higher knife-proof performance can be attained. The density of yarns in a woven fabric for use in a knife-proof material of the present invention is preferably 30/25 mm or more, more preferably 50/25 mm or more. When this density is low, the yarns tend to move, so that sufficient knife-proof performance sometimes can not be obtained. The weight of the fabric is preferably 100 g/m^2 or more, more preferably 150 g/m^2 or more, in order to achieve higher knife-proof performance. A part or a whole of the fabric of the present invention may be coated with or impregnated with a resin. The knife-proof material of the present invention is a lamination of such fabrics. Otherwise, such fabrics may be sewn integrally with a highly strong machine sewing thread for use as the knife-proof material.

The polybenzazole fibers of the present invention can be suitably used in a bullet-proof vest. The bullet-proof vest according to the present invention is made of a lamination of fabrics comprising the polybenzazole fibers. The texture of the woven fabric may be any of a plain weave

fabric, a twill fabric and other textures generally employed in fabrics. Preferably, a plain weave fabric or a twill fabric in which yarns are hard to move is employed to attain higher bullet-proof performance.

When the fineness of the polybenzazole fibers for use in the bullet-proof vest according to the present invention is as low as 1,110 dtex or less, preferably 600 dtex or less, higher bullet-proof performance can be attained. The density of yarns in a woven fabric for use in a bullet-proof vest of the present invention is preferably 40/25 mm or less. The weight of the fabric is preferably 200 g/m^2 or less, more preferably 150 g/m^2, in order to achieve higher bullet-proof performance. The bullet-proof vest of the present invention is made of a lamination of such fabrics. Otherwise, such fabrics may be sewn integrally with a highly strong machine sewing thread for use as the bullet-proof vest.

The polybenzazole fibers of the present invention can be suitably used in sail cloths. A sail cloth according to the present invention can be made of the polybenzazole fibers in combination with other high strength fibers such as polyethylene fibers, para-aramide fibers, wholly aromatic polyester fibers or carbon fibers. A sail cloth is reinforced in complicated directions. In the present invention, it is important to improve the durability of the polybenzazole fibers in the fiber axial direction, namely, the strength retention thereof when the polybenzazole fibers are exposed to an atmosphere of high temperature and high humidity over a long period of time.

EXAMPLES

Hereinafter, the present invention will be described

in more detail by way of Examples thereof. However, the following Examples should not be construed as limiting the scope of the present invention in any way, and may be appropriately modified unless they may be beyond the spirit of the present invention. Such modifications are also included in the scope of the present invention.

(Method of Twisting Filaments)

In accordance with the procedure of JIS-L1013, filaments were set on a twist tester, and were twisted under a given load determined by the following equation, so that the twist coefficient of the twisted yarn could be 30 at an interval of 50 cm between grips. The filaments were S-wise twisted and were left to stand alone for 30 seconds. Then, the twisted filaments were S-wise untwisted until the twist coefficient was decreased to 6. Thus, the sample S-twisted filaments having a twist coefficient of 6 was obtained. The equation for determining the given load (**a**) applied to the filaments being twisted, and the equation showing a relationship between the twist coefficient (K) and the number of twists (Tw) are shown below.

$\mathbf{a} = (1/10)D \quad K = 0.124 \times Tw \times D^{1/2}$

a: a given load (g)

Tw: number of twists (twisting times/inch)

D: the fineness of a filament (Dtex)

(Evaluation of Durability under Atmosphere of High temperature and High Humidity)

The durability of a filament against an atmosphere of high temperature and high humidity was evaluated based on the retention of the tensile strength of the filament found after a storage test under an atmosphere of high temperature and high humidity, relative to the tensile strength thereof found before the same test.

The sample filaments, twisted by the foregoing method (S-twisted yarn having a twist coefficient of 6), were wound onto a resinous bobbin with a diameter of 10 cm, and then were stored in an air-conditioned container under an atmosphere of high temperature and high humidity, and then were removed from the container.

Untreated filaments were subjected to a tensile test at a room temperature to measure the tensile strength thereof, which was expressed as **a** (cN/dtex). The sample twisted by the foregoing method (the S-twisted yarn having a twist coefficient of 6) was subjected to a tensile test at a room temperature to measure the tensile strength thereof, which was expressed as **b** (cN/dtex). The strength retention was determined by dividing the value **a** by the value **b** and multiplying the resultant quotient by 100. In this regard, Humidic Chamber 1G43M manufactured by Yamato Kagakusha was used in the above storage test. The sample was stored at a temperature of 80°C and a relative humidity of 80% for 240 hours in the air-conditioned container which was perfectly shielded from light. The tensile strength was measured with a tensile tester (AG-50KNG manufactured by SHIMADZU CORPORATION) according to the procedure of JIS-L1013.

(Evaluation of Concentrations of Phosphorus and Sodium Remaining in Filament)

The concentration of the residual phosphorus in the filament was determined by a colorimetric analysis according to the molybdenum blue method, after the sample had been subjected to a wet decomposition. The concentration of the residual sodium in the filament was determined as follows: the sample was carbonized and incinerated, and the resulting ash was dissolved in an acid

to form a 1.2N-HCl solution, from which the concentration of the residual sodium was determined by the atomic absorption method.

(Measurement of Diameter of Filament)

The diameter of a filament may be measured by an optical means or by a mechanical means such as a micrometer. In view of simplicity for measurement, the use of an optical means such as a scanning electron microscope (SEM), a laser type outer diameter measuring apparatus or the like is preferable. To reflect a whole of image of the population of filaments, it is needed to measure the diameters of as many single filaments as possible: the diameters of at least 5%, preferably 7% of the number of all filaments are measured. In many cases, the variation in the thickness of a polybenzazole filament in the lengthwise direction is larger than the variation in the thickness of polybenzazole filaments relative to each of the polybenzazole filaments. Accordingly, it is needed to measure the thickness of a filament in the lengthwise direction at a sufficient number of portions thereof. For this reason, the thickness of a filament with a length of at least 500 mm or more, preferably at least 750 mm or more in the lengthwise direction is measured at 25 mm or less intervals at most, preferably 12 mm or less intervals. When this interval is relatively long, there is a danger of missing the measurement of the diameter of a narrow and neck-in portion of the filament. In the investigation of the practical variation patterns, the variation in the diameter of a filament is very small when the measuring interval is less than 5 mm. In this point of view, the method of measuring the diameter of a single filament at 10 mm intervals over the 500 mm length of the filament is

employed in the present invention. The diameter of a single filament is measured at its several portion, using a scanning electron microscope (SEM) of a magnification of 5,000, and a standard deviation for assuming the average value and the normal distribution of the measured diameters is calculated, and a coefficient of variation (CV) is calculated by the following equation, using the standard deviation. The magnification of the scanning electron microscope is corrected by using latex beads with known diameters, before the measurement is conducted.

CV = a standard deviation [μm] of the diameter of a single filament/an average diameter [μm] of the single filament

(Evaluation of Durability of Sail Cloth under Atmosphere of High Temperature and High Humidity)

The durability of a sail cloth under an atmosphere of high temperature and high humidity was evaluated as follows. A sample of a sail cloth was stored in a container conditioned constantly at a high temperature and a high humidity. After that, the sample was taken out to a laboratory in a standard state (the temperature: 20 ± 2°C, and the relative humidity: 65 ± 2%), and was then subjected to a tensile test within 30 minutes thereafter, so that the retention of the tensile strength of the sample after the exposure to the atmosphere of high temperature and high humidity, relative to the tensile strength thereof before the same exposure was evaluated. Humidic Chamber 1G43M manufactured by Yamato Kagakusha was used for the storage test under the atmosphere of high temperature and high humidity. The storage test was continued for 240 hours in the above air-conditioned container which was perfectly

shielded from light and kept constant at 80°C and 80%RH. The tensile strength of the sample with a width of 2.5 cm was measured with a tensile tester (AG-50KNG manufactured by SHIMADZU CORPORATION) according to the procedure of JIS-L1096.

(Evaluation of Durability of Rubber-Reinforcing Cord or Composite Material under Atmosphere of High Temperature and High Humidity)

The durability of a sample of a rubber-reinforcing cord or a composite material under an atmosphere of high temperature and high humidity was evaluated as follows. The sample was stored in a container conditioned constantly at a high temperature and a high humidity. After that, the sample was taken out to a laboratory in a standard state (the temperature: 20 ± 2°C, and the relative humidity: 65 ± 2%), and was then subjected to a tensile test within 30 minutes thereafter, so that the retention of the tensile strength of the sample after the exposure to the atmosphere of high temperature and high humidity, relative to the tensile strength thereof before the same exposure was evaluated. Humidic Chamber 1G43M manufactured by Yamato Kagakusha was used for the storage test under the atmosphere of high temperature and high humidity. The storage test was continued for 240 hours in the above air-conditioned container which was perfectly shielded from light and kept constant at 80°C and 80%RH. The tensile strength of the sample was measured with a tensile tester (AG-50KNG manufactured by SHIMADZU CORPORATION) according to the procedure of JIS-L1013.

(Evaluation of Durability of High Strength Fiber Rope under Atmosphere of High Temperature and High Humidity)

The durability of a high strength fiber rope which was

not subjected to the foregoing twisting process was evaluated. The evaluation of the durability of the same under an atmosphere of high temperature and high humidity was made as follows. The rope was stored in a container conditioned constantly at a high temperature and a high humidity. After that, the rope was taken out to a laboratory in a standard state (the temperature: 20 ± 2°C, and the relative humidity: 65 ± 2%), and was then subjected to a tensile test within 30 minutes thereafter, so that the retention of the tensile strength of the rope after the exposure to the atmosphere of high temperature and high humidity, relative to the tensile strength thereof before the same exposure was evaluated. Humidic Chamber 1G43M manufactured by Yamato Kagakusha was used for the storage test under the atmosphere of high temperature and high humidity. The storage test was continued for 240 hours in the above air-conditioned container which was perfectly shielded from light and kept constant at 80°C and 80%RH. The strength retention of the rope was determined by measuring the tensile strengths of the rope found before and after the storage test, dividing the tensile strength after the storage test by the tensile strength before the same, and multiplying the quotient by 100.

(Evaluation of Durability of Woven or Knitted Fabric under Atmosphere of High Temperature and High Humidity)

The durability of a sample of a woven or knitted fabric under an atmosphere of high temperature and high humidity was evaluated as follows. The sample was stored in a container conditioned constantly at a high temperature and a high humidity. After that, the sample was taken out to a laboratory in a standard state (the temperature: 20 ±

2°C, and the relative humidity: 65 ± 2%), and was then subjected to a tensile test within 30 minutes thereafter, so that the retention of the tensile strength of the sample after the exposure to the atmosphere of high temperature and high humidity, relative to the tensile strength thereof before the same exposure was evaluated. Humidic Chamber 1G43M manufactured by Yamato Kagakusha was used for the storage test under the atmosphere of high temperature and high humidity. The storage test was continued for 240 hours in the above air-conditioned container which was perfectly shielded from light and kept constant at 80°C and 80%RH. The tensile strength of the woven fabric was measured according to the procedure of JIS-L1096, with a tensile tester (AG-50KNG manufactured by SHIMADZU CORPORATION), and the tensile strength of the knitted fabric was measured according to the procedure of JIS-L1018, with the same tensile tester.

(Making of Sample of Composite Material)

Filaments were unwound horizontally so as not to be twisted, and allowed to contact the surfaces of five stainless steel cylinders of ϕ 100 mm, alternately, so as to be opened. The opened filaments were allowed to contact a curved die which was shaped in a quarter of a circle with a semidiameter of 50 mm. A resin was discharged from a slit formed on the inlet of the curved die, in the forwarding direction of the running filaments, to thereby coat the filaments with the resin. The filaments under a tension were run over the curved surface of the die, to have a shearing resistance so as to be impregnated with the resin. After that, the filaments impregnated with the resin were allowed to pass through a die having an inlet and a nozzle, and cooled to obtain a rod-like composite

material. Fig. 1 shows an example of this resin-impregnating system with the die. As the resin, an ethylene-vinyl alcohol copolymer "EVAL (R)" (105B) manufactured by KURARAY CO., LTD. was used. The die used had an inlet angle of 30°, a nozzle with a diameter of 0.6 mm ϕ, and a parallel portion with a length of 0.5 mm.

(Evaluation of Durability of Spun Yarn under Atmosphere of High Temperature and High Humidity)

The durability of a spun yarn which was not subjected to a twisting process was evaluated. The spun yarn wound onto a resinous bobbin was stored in a container conditioned constantly at a high temperature and a high humidity. After that, the sample was taken out and then subjected to a tensile test at a room temperature. The resultant tensile strength was divided by a tensile strength of a spun yarn which was not subjected to the above storage test, and the resultant quotient was multiplied by 100 to obtain a strength retention. Humidic Chamber 1G43M manufactured by Yamato Kagakusha was used for the storage test under the atmosphere of high temperature and high humidity, as well as in the evaluation of the filaments before cutting. The storage test was continued for 240 hours in the above air-conditioned container which was perfectly shielded from light and kept constant at 80°C and 80%RH. The tensile strength of the spun yarn with a length of 200 mm was measured according to the procedure of JIS-L1095, with a tensile tester (AG-50KNG manufactured by SHIMADZU CORPORATION).

(Example 1)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g), terephthalic

acid (260.8 g) and 122% polyphosphoric acid (2,078.2 g) were stirred at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 135°C for 25 hours, at 150°C for 5 hours and at 170°C for 20 hours. Threne (14.8 g) was added to the resultant poly(p-phenylenebenzobisoxazole) dope (2.0 kg) having an intrinsic viscosity of 29 dL/g at 30°C, measured using a methanesulfonic acid solution, and the mixture was stirred.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant polybenzazole filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,600 ppm, and that of sodium was 3,600 ppm; and the molar ratio of Na/P was 1.05.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 86%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 87%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 89%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers.

Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 87%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,220 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 86%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,660 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 85%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 135 g/m^2. The tensile strength of

the fabric in the warp yarn direction was 5,850 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 84%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.29 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 82%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 15.3 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 84%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 135 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,600 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

(Example 2)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g), terephthalic acid (260.8 g) and 122% polyphosphoric acid (2,078.2 g) were stirred at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 135°C for 25 hours, at 150°C for 5 hours and at 170°C for 20 hours. Copper phthalocyanine (14.8 g) was added to the resultant poly(p-phenylenebenzobisoxazole) dope (2.0 kg) having an intrinsic viscosity of 30 dL/g at 30°C, measured using a methanesulfonic acid solution, and the mixture was stirred.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 120 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the

foregoing methods. As a result, the concentration of phosphorous was 4,500 ppm, and that of sodium was 2,400 ppm; and the molar ratio of Na/P was 0.72.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 83%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 82%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 85%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 85%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,250 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,660 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 80%.

Further, the polybenzazole fiber yarns thus obtained

were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 134 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,890 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.30 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 80%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 14.8 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 81%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 136 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,580 N/3 cm.

The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 80%.

(Example 3)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g), terephthalic acid (260.8 g) and 122% polyphosphoric acid (2,078.2 g) were stirred at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 135°C for 25 hours, at 150°C for 5 hours and at 170°C for 20 hours. Copper phthalocyanine (14.8 g) was added to the resultant poly(p-phenylenebenzobisoxazole) dope (2.0 kg) having an intrinsic viscosity of 30 dL/g at 30°C, measured using a methanesulfonic acid solution, and the mixture was stirred.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with

water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,400 ppm, and that of sodium was 3,600 ppm; and the molar ratio of Na/P was 1.10.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 88%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 90%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating

temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 91%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 90%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,250 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 87%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,670 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high

temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 85%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 136 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,800 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 86%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.30 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 87%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 15.8 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 85%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with

30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 135 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,620 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 85%.

(Example 4)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g), terephthalic acid (260.8 g) and 122% polyphosphoric acid (2,078.2 g) were stirred at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 135°C for 25 hours, at 150°C for 5 hours and at 170°C for 20 hours. Copper phthalocyanine (14.8 g) was added to the resultant poly(p-phenylenebenzobisoxazole) dope (2.0 kg) having an intrinsic viscosity of 30 dL/g at 30°C, measured using a methanesulfonic acid solution, and the mixture was stirred.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous

bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 3 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,700 ppm, and that of sodium was 5,400 ppm; and the molar ratio of Na/P was 1.55.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 86%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 86%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the

first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 87%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 88%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,190 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 84%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction.

The tensile strength of the tubular knitted fabric in the vertical direction was 1,660 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 135 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,700 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.30 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 83%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 15.1 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 84%.

Further, two polybenzazole filaments thus obtained

were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 136 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,550 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

(Example 5)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g), terephthalic acid (260.8 g) and 122% polyphosphoric acid (2,078.2 g) were stirred at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 135°C for 25 hours, at 150°C for 5 hours and at 170°C for 20 hours. Copper phthalocyanine (4.4 g) was added to the resultant poly(p-phenylenebenzobisoxazole) dope (2.0 kg) having an intrinsic viscosity of 30 dL/g at 30°C, measured using a methanesulfonic acid solution, and the mixture was stirred.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments

were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,500 ppm, and that of sodium was 4,000 ppm; and the molar ratio of Na/P was 1.20.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 81%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 82%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were

S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 83%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 81%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,300 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

Further, the spun yarns with a cotton yarn count of

20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,740 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 133 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,920 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 80%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.29 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 79%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 14.5 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high

humidity was evaluated. As a result, the strength retention of the spun yarn was 80%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 133 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,690 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 79%.

(Example 6)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g), terephthalic acid (260.8 g) and 122% polyphosphoric acid (2,078.2 g) were stirred at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 135°C for 25 hours, at 150°C for 5 hours and at 170°C for 20 hours. Copper phthalocyanine (32.5 g) was added to the resultant poly(p-phenylenebenzobisoxazole) dope (2.0 kg) having an intrinsic viscosity of 30 dL/g at 30°C, measured using a methanesulfonic acid solution, and the mixture was stirred.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air

gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,400 ppm, and that of sodium was 3,400 ppm; and the molar ratio of Na/P was 1.04.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 87%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 89%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 85%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 88%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,010 N/3 cm. Then, the durability of the fabric under an atmosphere of high

temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 87%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,590 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 85%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 138 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,610 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 86%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.31 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 85%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a

cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 15.5 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 85%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 138 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,280 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 84%.

(Example 7)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g) and terephthalic acid (252.7 g) were added in 122% polyphosphoric acid (2,165.5 g) with stirring at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 120°C for 4 hours, at 135°C for 20 hours and at 150°C for 5 hours. Further, to the resultant oligomer dope, a dispersion obtained by adding terephthalic acid (5.6 g) and copper phthalocyanine (19.5 g) in 122% polyphosphoric acid (74.4 g) was added, and the mixture was allowed to react at 170°C for 5 hours and at 200°C for 10 hours to obtain poly(p-phenylenebenzobisoxazole) dope having an intrinsic viscosity of 29 dL/g at 30°C, measured using a methanesulfonic acid solution.

After that, the resultant dope was spun to make

filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 120 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,600 ppm, and that of sodium was 2,400 ppm; and the molar ratio of Na/P was 0.70.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 84%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination

was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 81%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 86%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 86%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne.

Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,240 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,690 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 136 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,820 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was

0.29 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 81%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 15.0 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 83%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 135 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,500 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 80%.

(Example 8)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g) and terephthalic acid (252.7 g) were added in 122% polyphosphoric acid (2,165.5 g) with stirring at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 120°C for 4 hours, at 135°C for 20 hours and at 150°C for 5 hours. Further, to the resultant oligomer dope, a dispersion obtained by adding terephthalic acid (5.6 g) and copper phthalocyanine (19.5 g) in 122% polyphosphoric

acid (74.4 g) was added, and the mixture was allowed to react at 170°C for 5 hours and at 200°C for 10 hours to obtain poly(p-phenylenebenzobisoxazole) dope having an intrinsic viscosity of 29 dL/g at 30°C, measured using a methanesulfonic acid solution.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,900 ppm, and that of sodium was 4,200 ppm; and the molar ratio of Na/P was 1.15.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 89%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 88%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 91%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope

under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 92%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,210 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 88%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,660 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 85%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 135 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,780 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result,

the strength retention of the fabric was 86%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.30 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 89%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 16.0 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 86%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 136 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,480 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 84%.

(Example 9)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g) and

terephthalic acid (252.7 g) were added in 122% polyphosphoric acid (2,165.5 g) with stirring at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 120°C for 4 hours, at 135°C for 20 hours and at 150°C for 5 hours. Further, to the resultant oligomer dope, a dispersion obtained by adding terephthalic acid (5.6 g) and copper phthalocyanine (19.5 g) in 122% polyphosphoric acid (74.4 g) was added, and the mixture was allowed to react at 170°C for 5 hours and at 200°C for 10 hours to obtain poly(p-phenylenebenzobisoxazole) dope having an intrinsic viscosity of 29 dL/g at 30°C, measured using a methanesulfonic acid solution.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 3 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in

the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,800 ppm, and that of sodium was 5,600 ppm; and the molar ratio of Na/P was 1.15.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 86%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 84%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature

and high humidity was 86%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 88%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,150 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 85%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,670 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 136 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,790 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.30 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 82%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 15.0 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 84%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 135 g/m^2. The tensile strength of

the fabric in the warp yarn direction was 5,560 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

(Example 10)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g) and terephthalic acid (252.7 g) were added in 122% polyphosphoric acid (2,165.5 g) with stirring at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 120°C for 4 hours, at 135°C for 20 hours and at 150°C for 5 hours. Further, to the resultant oligomer dope, a dispersion obtained by adding terephthalic acid (5.6 g) and copper phthalocyanine (5.6 g) in 122% polyphosphoric acid (74.4 g) was added, and the mixture was allowed to react at 170°C for 5 hours and at 200°C for 10 hours to obtain poly(p-phenylenebenzobisoxazole) dope having an intrinsic viscosity of 30 dL/g at 30°C, measured using a methanesulfonic acid solution.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the

residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,500 ppm, and that of sodium was 3,800 ppm; and the molar ratio of Na/P was 1.14.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 82%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 81%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord.

The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 82%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 84%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,380 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular

knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,760 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 135 g/m^2. The tensile strength of the fabric in the warp yarn direction was 6,040 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 81%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.30 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 78%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 14.6 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength

retention of the spun yarn was 81%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 134 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,770 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 78%.

(Example 11)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g) and terephthalic acid (252.7 g) were added in 122% polyphosphoric acid (2,165.5 g) with stirring at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 120°C for 4 hours, at 135°C for 20 hours and at 150°C for 5 hours. Further, to the resultant oligomer dope, a dispersion obtained by adding terephthalic acid (5.6 g) and copper phthalocyanine (41.1 g) in 122% polyphosphoric acid (74.4 g) was added, and the mixture was allowed to react at 170°C for 5 hours and at 200°C for 10 hours to obtain poly(p-phenylenebenzobisoxazole) dope having an intrinsic viscosity of 28 dL/g at 30°C, measured using a methanesulfonic acid solution.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and

solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,800 ppm, and that of sodium was 3,900 ppm; and the molar ratio of Na/P was 1.09.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 87%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an

atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 87%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 88%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 89%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft

yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,380 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 86%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,560 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 85%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 138 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,590 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 86%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.29 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 85%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 15.3 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 85%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 137 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,310 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 84%.

(Example 12)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g), terephthalic acid (260.8 g), quinacridone (19.2 g) and 122% polyphosphoric acid (2,078.2 g) were stirred at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 135°C for 25 hours, at 150°C for 5 hours and at 170°C for 20 hours to obtain poly(p-phenylenebenzobisoxazole) dope having an intrinsic viscosity of 24 dL/g at 30°C, measured using a methanesulfonic acid solution.

After that, the resultant dope was spun to make filaments each singly having a diameter of 11.5 μm and a

fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,900 ppm, and that of sodium was 3,900 ppm; and the molar ratio of Na/P was 1.07.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 85%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination was cured and dried to make a sail cloth. The sail cloth

was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 83%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 84%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 87%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne. Two such spun yarns were twisted to make a two ply yarn

with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,120 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 84%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,610 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 83%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 136 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,830 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 81%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was 0.30 in terms of the volume ratio. The durability of the

composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 82%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 15.0 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 84%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 135 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,500 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 82%.

(Comparative example 1)

Under a stream of a nitrogen gas, 4,6-diaminoresorcinol dihydrochloride (334.5 g), terephthalic acid (260.8 g) and 122% polyphosphoric acid (2,078.2 g) were stirred at 60°C for one hour, and the mixture was gradually heated so as to be reacted at 135°C for 25 hours, at 150°C for 5 hours and at 170°C for 20 hours to obtain poly(p-phenylenebenzobisoxazole) dope having an intrinsic viscosity of 30 dL/g at 30°C, measured using a methanesulfonic acid solution.

After that, the resultant dope was spun to make

filaments each singly having a diameter of 11.5 μm and a fineness of 1.5 denier. That is, the dope was extruded through a nozzle having 166 holes with diameters of 0.18 mm at 175°C to make the filaments, which were then dipped and solidified in a first washing bath so located as to converge the filaments at an appropriate position to make a multi-filament. A quench chamber was provided in an air gap between the nozzle and the first washing bath, so that the filaments could be drawn long at an uniform temperature. The quench temperature was 65°C. After that, the filaments were washed with water until the concentration of the residual phosphorous in the polybenzazole filaments reached 5,000 ppm or less, and were then wound onto resinous bobbins without drying. The take-up rate was 200 m/minute.

The wound filament was neutralized with a 1% aqueous NaOH solution for 10 seconds, and was then washed with water for 15 seconds, followed by drying at 80°C for 4 hours. The concentrations of phosphorous and sodium remaining in the resultant filaments were measured by the foregoing methods. As a result, the concentration of phosphorous was 4,400 ppm, and that of sodium was 4,000 ppm; and the molar ratio of Na/P was 1.22.

The durability of the filament under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention thereof was 77%.

Six polybenzazole filaments thus obtained were doubled but not twisted to make a yarn having a total fineness of 1,500 deniers. Such yarns were used to make a scrim filled with 5 warp yarns/inch and 5 weft yarns/inch. The scrim was sandwiched between two biaxially oriented polyester films with thickness of 12 microns on each of which a polyurethane-based adhesive was applied, and the lamination

was cured and dried to make a sail cloth. The sail cloth was cut out to obtain a cloth strip with a width of 2.5 cm and a length of 50 cm, which included five reinforcing yarns. The durability of the cloth strip under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the cloth strip was 76%.

Otherwise, six polybenzazole filaments thus obtained were Z-wise twisted at a rate of 32 T/10 cm to make a Z-twisted yarn. Two Z-twisted yarns obtained as above were S-wise twisted at a rate of 32 T/10 cm to make a crude cord. The crude cord was subjected to a two-staged dipping treatment to make a dip cord. The dipping liquid for the first stage was an aqueous dispersion of an epoxy resin, and the treating temperature was 240°C. The dipping liquid for the second stage was a RFL liquid, and the treating temperature was 235°C. The strength retention of the resultant dip cord under an atmosphere of high temperature and high humidity was 78%.

Otherwise, twelve polybenzazole filaments thus obtained were twisted at a rate of 80 T/1 m to make a twisted union yarn having a thickness of 3,000 deniers. Eight twisted union yarns thus obtained were braided with a conventional machine to make a rope filled with the eight twisted union yarns. The durability of the resultant rope under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the rope was 78%.

Otherwise, the polybenzazole filaments thus obtained were cut into staple fibers with lengths of 51 mm. The resultant staple fibers were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20/1 Ne.

Two such spun yarns were twisted to make a two ply yarn with a cotton yarn count of 20/2 Ne.

The two ply yarns thus obtained were woven to make a 2/1 twill fabric filled with 68 warp yarns/inch and 60 weft yarns/inch. The tensile strength of the resultant fabric in the vertical direction was 4,270 N/3 cm. Then, the durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 72%.

Further, the spun yarns with a cotton yarn count of 20/1 Ne obtained as above were knitted to make a tubular knitted fabric filled with 68 stitches/inch in the vertical direction and 29 stitches/inch in the lateral direction. The tensile strength of the tubular knitted fabric in the vertical direction was 1,590 N/5 cm. Then, the durability of the tubular knitted fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 70%.

Further, the polybenzazole fiber yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 60 warp yarns/inch and 60 weft yarns/inch. The weight of the fabric was 134 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,780 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 73%.

Further, four polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn having a total fineness of 1,000 deniers. The yarns thus obtained were used to make a composite material by the foregoing method for making the sample of a composite material. The content of the filaments in the resultant composite material was

0.30 in terms of the volume ratio. The durability of the composite material under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the composite material was 73%.

Further, the staple fibers with lengths of 51 mm, cut from the polybenzazole filaments thus obtained, were spun at a twist coefficient of 3.5 to make a spun yarn with a cotton yarn count of 20 Ne. The tensile strength of the spun yarn was 9.3 cN/dtex. The durability of the spun yarn under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the spun yarn was 75%.

Further, two polybenzazole filaments thus obtained were doubled but not twisted, to make a yarn with a thickness of 555 dtex. The yarns thus obtained were woven with a rapier loom to make a plain weave fabric filled with 30 warp yarns/inch and 30 weft yarns/inch. The weight of the resultant fabric was 133 g/m^2. The tensile strength of the fabric in the warp yarn direction was 5,540 N/3 cm. The durability of the fabric under an atmosphere of high temperature and high humidity was evaluated. As a result, the strength retention of the fabric was 71%.

The foregoing results are summarized in Tables 1-3. As is apparent from these Tables, the polybenzazole fibers of each Example and the articles made thereof had a good durabilities under an atmosphere of high temperature and high humidity, as compared with the polybenzazole fibers of Comparative Example and the articles made thereof.

Table 1

	Kinds of pigment	Polybenzazole fiber						
		Content of pigment in filament	Initial strength of filament	CV	Concentration of phosphorous in filament	Concentration of sodium in filament	Na/P (Molar ratio)	Durability under an atmosphere of high temperature and high humidity
		%	GPa	-	ppm	ppm	-	%
Example 1	Threne	5.0	5.8	0.047	4600	3600	1.05	86
Example 2	Copper phthalocyanine	5.0	5.9	0.036	4500	2400	0.72	83
Example 3	Copper phthalocyanine	5.0	5.9	0.034	4400	3600	1.10	88
Example 4	Copper phthalocyanine	5.0	5.8	0.040	4700	5400	1.55	86
Example 5	Copper phthalocyanine	1.5	6.0	0.047	4500	4000	1.20	81
Example 6	Copper phthalocyanine	10	5.6	0.062	4400	3400	1.04	87
Example 7	Copper phthalocyanine	5.0	5.9	0.057	4600	2400	0.70	84
Example 8	Copper phthalocyanine	5.0	5.8	0.043	4900	4200	1.15	89
Example 9	Copper phthalocyanine	5.0	5.8	0.039	4800	5600	1.57	86
Example 10	Copper phthalocyanine	1.5	6.1	0.031	4500	3800	1.14	82
Example 11	Copper phthalocyanine	10	5.5	0.059	4800	3900	1.09	87
Example 12	Quinacridone	5.0	5.7	0.039	4900	3900	1.07	85
Comparative Example 1	—	0	6.3	0.028	4400	4000	1.22	77

Table 2

	Sail cloth	Dip cord	Rope	Woven fabric (Twill fabric)		Knitted fabric (Tubular fabric)		Woven fabric (Plain weave fabric, for knife-proof material)		
	Durability	Durability	Durability	Fabric property	Durability	Fabric property	Durability	Fabric property	Weight	Durability
	%	%	%	N/3cm	%	N/5cm	%	N/3cm	g/m²	%
Example 1	87	89	87	4220	86	1660	85	5850	135	84
Example 2	82	85	85	4250	82	1710	80	5890	134	82
Example 3	90	91	90	4250	87	1670	85	5800	136	86
Example 4	86	87	88	4190	84	1660	83	5700	135	83
Example 5	82	83	81	4300	83	1740	83	5920	133	80
Example 6	89	85	88	4010	87	1590	85	5610	138	86
Example 7	81	86	86	4240	83	1690	82	5820	136	82
Example 8	88	91	92	4210	88	1660	85	5780	135	86
Example 9	84	86	88	4150	85	1670	83	5790	136	82
Example 10	81	82	84	4380	82	1760	83	6040	135	81
Example 11	87	88	89	3990	86	1560	85	5590	138	86
Example 12	83	84	87	4120	84	1610	83	5830	136	81
Comparative Example 1	76	78	78	4270	72	1590	70	5780	134	73

Table 3

	Composite material		Spun yarn		Woven fabric (Plain weave fabric, for bullet-proof material)		
	Content of filaments in composite material	Durability	Initial strength of filament	Durability	Fabric property	Weight	Durability
	Volume ratio	%	cN/dtex	%	N/3cm	g/m²	%
Example 1	0.29	82	15.3	84	5600	135	83
Example 2	0.30	80	14.8	81	5580	136	80
Example 3	0.30	87	15.8	85	5620	135	85
Example 4	0.30	83	15.1	84	5550	136	82
Example 5	0.29	79	14.5	80	5690	133	79
Example 6	0.31	85	15.5	85	5280	138	84
Example 7	0.29	81	15	83	5500	135	80
Example 8	0.30	89	16	86	5480	136	84
Example 9	0.30	82	15	84	5560	135	82
Example 10	0.30	78	14.6	81	5770	134	78
Example 11	0.29	85	15.3	85	5310	137	84
Example 12	0.30	82	15	84	5500	135	82
Comparative Example 1	0.30	73	9.3	75	5540	133	61

INDUSTRIAL APPLICABILITY

According to the present invention, there can be provide polybenzazole fibers which can sufficiently maintain the strength thereof even when exposed to an atmosphere of high temperatures and high humidity for a long period of time after yarns made thereof have had kink bands therein. Therefore, the use of the polybenzazole fibers can enhance the practical performance in the applications where the fibers are processed to woven fabrics, knitted fabrics, braids, ropes, cords and the like, which include, for example, tension materials such as cables, tension members (electric wires, optical fibers and the like) and ropes, high shock-proof members such as bullet-proof materials, cutting-proof members such as gloves, rubber-reinforcing materials such as belts, tires, shoe soles, ropes and hoses.